A novel approach to lead isotope provenance studies of tin and bronze: applications to South African, Botswanan and Romanian artifacts

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ABSTRACT

Lead isotopic ratios of cassiterite, the dominant ore of tin, evolve after crystallization through decay of uranium (U) and thorium (Th) to lead (Pb), due to the relatively elevated U/Pb ratios of this mineral. We show that the Pb isotopic ratios of smelted tin at Rooiberg, South Africa, form an isochron with a model age that matches the known geological age (~2 Ga) of the host granite for the Rooiberg cassiterite deposits. Since the Pb isotopic ratios of many prehistoric tin and bronze artifacts throughout southern Africa also fall on this isochron, we deduce that they were made with tin from either the Rooiberg deposits or similar age deposits that exist nearby. In addition, we show that bronze artifacts from Romania define an isochron corresponding to a Variscan age (~0.3 Ga), suggesting a central or western European tin deposit as its source, since no Variscan tin is known from the neighboring Carpathian Mountains. Implications of this approach for provenance studies of tin and bronzes around the world are examined given various major tin deposits and their age distribution.

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1. Introduction

One of the major unsolved questions in the later archaeology of the Old World is the source (or sources) of tin for the Bronze Age of the Near East and the eastern Mediterranean — both of which lack major tin deposits. This has been intensely debated since J.D. Muhly's comprehensive survey of the geological, historical, and archaeological evidence for the origin of tin metal in antiquity (Muhly, 1973). The majority of tin must have been obtained through long-distance trade, but there is considerable disagreement over potential sources and trade routes (e.g., Franklin et al., 1979; Muhly, 1985; Yener et al., 1989; Pigott, 1999; Yener, 2000; Weeks, 2003; Nezafati et al., 2006).

When compared to the many published provenance studies of copper alloy artifacts, there has been remarkably little archaeometric study of the provenance of ancient tin. Rapp and colleagues (Rapp, 1978; Rothe and Rapp, 1995; Rapp et al., 1999) attempted to use trace elements to characterize deposits of cassiterite (the main tin ore) and tin metal produced from cassiterite. However, to our knowledge, this approach has only been used in one other archaeological provenance study of the earliest known tin artifacts from Thermi on Lesbos (Begemann et al., 1992). Other studies have attempted to use tin isotopes to characterize tin sources, although researchers commonly found that either the variations in tin isotopic ratios from different regions was quite small and/or barely larger than the analytical error (Gale, 1997; Begemann et al., 1999; Yi et al., 1999; Clayton et al., 2002; Nowell et al., 2002). Lastly, there are few published measurements of Pb isotopic ratios in cassiterite or in prehistoric tin metal. This runs in stark contrast to the thousands of published Pb isotopic ratios for copper ores and for prehistoric copper and copper alloys.

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Lead isotopic ratios have been measured for many hundreds of bronze artifacts from the Mediterranean, Europe and western Asia (e.g., Gale and Stos-Gale, 1982; Pernicka et al., 1997; Rohl and Needham, 1998; Weeks, 2003). Since these have without exception been compared to Pb isotopic data for copper sources (or to lead sources in the case of leaded bronzes), most researchers to date have implicitly assumed that the lead in bronze must derive primary from the copper, or from added lead, rather than from the tin (Gale and Stos-Gale, 1982; Gale et al., 1985).

In this article, we call attention to the fact that the Pb isotopic signature of cassiterite can serve as a unique fingerprinting tool for the tin in both tin and bronze artifacts. Specifically, cassiterite is unique from many other metal ores (e.g., sulfides) because it commonly contains significantly larger concentrations of U relative to Pb. As a result, the Pb isotopic composition of cassiterite can be dominated by the Pb produced by the radioactive decay of U over time, rather than the Pb initially incorporated into the mineral. This makes cassiterite a potentially valuable mineral for direct U–Pb dating of ore deposits, although it has not been used for this purpose, partly because it is extremely difficult to fully dissolve cassiterite with acids (Gulson and Jones, 1992; Yuan et al., 2008). Here, we show that the tin metal smelted from old cassiterite deposits maintains the Pb isotopic signature of the cassiterite ore, and thus, that one can apply U–Pb isochron dating (Faure and Mensing, 2005) to "fingerprint" individual tin provinces. We suggest that under favorable instances, the contribution of relatively radiogenic Pb from tin can be used to tease out a "ghost" age of the tin metallogenetic province. Even if a specific ore deposit is not decipherable with this tool, the rarity and unusual provinciality of tin deposits around the globe may make identification of the tin metallogenetic province an important tool for understanding metal trades in bronze artifacts from antiquity.

1.1. Lead isotopic ratios of cassiterite − the geochemical basis

Lead has four stable isotopes − ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb − all of which were present at the time of earth's formation. The latter three are also the products of the radioactive decay of their parent isotopes − ^{238}U (half life 4.468 Gyr), ^{235}U (703.8 Myr), and ^{232}Th (14.01 Gyr) − respectively. The isotopic composition of lead in the Earth as a whole at any given time is the sum of the lead present at the time of its formation and lead that has been produced subsequently by radioactive decay. The Earth, however, is not isotopically homogeneous, but has separated into crust, mantle, and core, each with different initial U/Pb ratios. Each of these reservoirs subsequently evolved further by the additional decay of U and Th to Pb to acquire diverse, and unique, Pb isotopic compositions (Stacey and Kramers, 1975).

When a mineral crystallizes from a melt, and incorporates lead into its crystal structure, it acquires the Pb isotopic composition of its parent reservoir. This is called "common lead" (Faure and Mensing, 2005). If the mineral lattice cannot accommodate U and Th (and therefore cannot gain lead by radioactive decay over time) the "common lead" isotopic ratios will be preserved indefinitely, unless subsequent processes result in the addition or loss of Pb, or the addition of U and Th. Copper, lead, and silver sulfide minerals incorporate Pb, but generally cannot accommodate U and Th in their crystal lattices. Thus these minerals retain their "common lead" isotopic signatures from the time of their formation.

The use of Pb isotopic ratios in metal provenance studies is founded on the prerequisite that ore deposits can be clearly distinguished from each other (Lambert and Ruiz, 1999). In practice, this means that, within a given area, the variation in isotopic ratios within individual deposits of "common lead" minerals should be smaller than the variation in ratios between deposits. Ideally

isotope ratios for a given ore deposit on bivariate plots (e.g., ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb) will cluster tightly, providing a "fingerprint" for that deposit that is separated from equally tight clusters for other deposits. Archaeologists can then match the isotopic ratios of individual archaeological artifacts to the "fingerprints" of their parent ore sources (e.g., Gale and Stos-Gale, 1982; Thibodeau et al., 2007). Although there are often practical difficulties with this approach, including overlapping fingerprints of two or more sources, mixing of metal from different sources, and metal recycling (Budd et al., 2000; Pernicka, 1995; Pollard, 2009), the lead fingerprinting approach has been successfully applied to many ancient copper, lead, and silver artifacts primarily to rule out certain metal sources and support various hypotheses of positive correlations between an ore deposit and a metal artifact.

This approach works well for minerals that have "common lead" isotopic signatures. However, some minerals do accommodate significant amounts of U and Th upon crystallization, and therefore have Pb isotopic ratios that evolve over time as a result of radioactive decay of U and Th to radiogenic ^{208}Pb, ^{207}Pb and ^{206}Pb. Cassiterite (SnO_2) is one such mineral. Cassiterite accepts very little lead upon crystallization because the charge and ionic radius for the common lead ion in aqueous solutions (Pb^{2+}, 119 pm) are substantially different from those of octahedrally-coordinated Sn^{4+} (83 pm). In contrast, U^{4+} (103 pm), Th^{4+} (108 pm), and U^{6+} (89 pm) are better able to substitute for Sn in the cassiterite lattice, and thus may be present in significantly higher concentrations (up to several hundred ppm) than the Pb^{2+} ion in cassiterite (Farthing, 2002).

As a result of the incorporation of U and Th, ratios of radiogenic Pb isotopes to ^{204}Pb in cassiterites from a single deposit exhibit a much larger range than those in "common lead" minerals like galena or chalcopyrite. Published ^{206}Pb/^{204}Pb ratios for "common lead" minerals fall within the range of 15−22, but, as we show below, ^{206}Pb/^{204}Pb ratios of tin smelted from a cassiterite deposit that crystallized two billion years ago can range from less than 20 to over 90. Thus the traditional isotopic "fingerprinting" method used for archaeological provenance studies of copper alloys, silver and lead artifacts cannot be used for provenance studies of tin artifacts smelted from old cassiterites − because ratios of any of the three radiogenic isotopes to ^{204}Pb do not produce the tight clusters typical of single-stage deposits of "common lead" minerals.

However, on a plot of ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb, all cassiterite crystals that crystallized at the same time from a single parent ore fluid will fall on a straight line (an isochron), with a uniform slope that equals the ratio of radiogenic ^{207}Pb to radiogenic ^{206}Pb. The slope of the isochron can then be used to calculate the age of the deposit:

$$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\text{radiogenic} = \frac{^{235}\text{U}(e^{\lambda_2 t} - 1)}{^{238}\text{U}(e^{\lambda_1 t} - 1)} \tag{1}$$

Where:

^{235}U/^{238}U = the present day ratio of ^{235}U to ^{238}U
λ_2 = decay constant for ^{235}U
λ_1 = decay constant for ^{238}U
t = time elapsed since crystallization of the ore deposit
(Faure and Mensing, 2005)

Three calculated reference (i.e., synthetic) isochrons for hypothetical cassiterite deposits of ages 325 million years, 1.2 billion years, and 2 billion years are shown in Fig. 1. Each isochron is calculated from points representing crystals with different initial ratios of U to Pb, varying from 0 to 5. Crystals with the highest initial U to Pb ratios plot at the top right end of each isochron. Thus
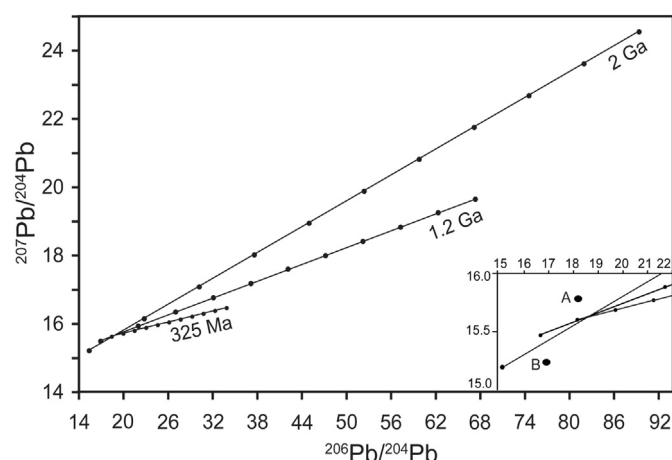
Fig. 1. Three reference isochrons for hypothetical cassiterite deposits of ages 325 million, 1.2 billion, and 2 billion years. Slopes are calculated with Equation (1), and isochrons are anchored by the "common lead" isotopic ratios estimated by the Stacey–Kramers model for ore deposits of their respective age. Each isochron contains ten points representing the radiogenic lead isotopic ratios produced by hypothetical cassiterite crystals with U/Pb ratios of 0 (bottom left-most point) to 5 (top right point). At bottom right is an enlarged section of the common-lead isotopic region. Hypothetical points A and B clearly do not lie on the isochrons, and must therefore originate from a different tin source, or be the product of mixing of two or more sources.

the isochron itself is the "fingerprint" of a given cassiterite deposit. Gulson and Jones (1992) and Yuan et al. (2008) have successfully obtained isochrons from measured values of Pb isotopic ratios in cassiterite.

Because Pb isotopes do not fractionate during smelting (Gale and Stos-Gale, 1996), tin artifacts produced from a single cassiterite deposit should in theory produce the same isochron as the cassiterite ore (assuming that the smelted tin has not picked up any lead from fuels, slags, and refractories during smelting). Determining the geological provenance of a given tin artifact is then simply a matter of matching the ^{207}Pb/^{204}Pb and ^{206}Pb/^{204}Pb ratios of the artifact to the reference isochrons of potential sources. Tin artifacts that plot off the isochrons (for example, the hypothetical points A and B in the enlarged portion of Fig. 1) must originate from other sources, or be the product of mixing of materials from two or more sources. Of note, young cassiterite deposits (<100 Ma) should display Pb isotopic signatures that have not evolved appreciably from that of the initial "common lead" that they incorporated, making an isochron more difficult, if not impossible, to identify.

Although cassiterite deposits of the same age will produce isochrons with the same slope, they may have had different initial isotopic ratios of "common lead". In Fig. 1, each reference isochron was anchored by the "common lead" values predicted by the Stacey–Kramers model for deposits of that age (Stacey and Kramers, 1975). But Stacey–Kramers is an idealized model for the Pb isotopic composition of a "bulk" earth reservoir at any given time, and most real geologic reservoirs within the earth's crust possess Pb isotopic compositions that depart from the predictions of the Stacey–Kramers model. Fig. 2 shows calculated reference isochrons for three deposits that all formed 1.2 billion years ago, but from isotopically distinct geologic reservoirs with different initial "common lead" values (points A, B and C). Consequently, cassiterite deposits that formed at the same time may have distinctly different, but parallel isochrons.

Ultimately, the Pb isotopic signature of bronzes comprises a mixture of the signatures of the two sources of Pb: the copper and the tin. Due to low U/Pb ratios of copper minerals (mostly sulfides), the copper source will have Pb isotopic ratios very close to the initial "common lead" of the reservoir. In contrast, the tin source

may have higher radiogenic Pb isotopic ratios due to additional Pb formed from the decay of U and Th since the formation of the parent ore cassiterite. The concentration of Pb in the copper and tin components is also a critical factor in determining the final Pb isotopic ratios of the bronze mixture. Cassiterite will always have relatively low concentrations (few ppm) of Pb, due to the crystal chemistry considerations mentioned above. However, copper sulfide ore can contain significantly higher concentrations (over several hundred ppm) of Pb. It follows that the ability to see the Pb isotopic signature of the tin in bronze objects depends on how Pb-depleted the copper source was. Only low Pb bronzes are likely to yield isochrons that reflect the tin component; in high Pb bronzes, the copper-ore end member will dominate the Pb signal.

2. Samples

2.1. Tin ingots and bronzes from Southern Africa

Some two dozen cast tin ingots of distinctive shapes, and two shapeless lead–tin lumps, have been recovered over the last hundred years from surface contexts and archaeological excavations within a large area of northern South Africa, eastern Botswana and southern Zimbabwe (Fig. 3). Prehistoric tin workings discovered in this region are well known from the Rooiberg valley, where many shallow workings (up to 60 m deep) are estimated to have produced some 2×10^6 kg of tin ore before ca. 1850 AD (Recknagel, 1908; Baumann, 1919; Chirikure et al., 2007, 2010). The ores are composed of pockets, stratiform lodes, and near-vertical fracture fillings of cassiterite, tourmaline, and carbonates (siderite or ankerite), with abundant pyrite and other sulfides (mostly chalcopyrite, with rare galena and scheelite) (Leube and Stumpfl, 1963; Rozendaal et al., 1995; Crocker et al., 2001; Labuschagne, 2004). The tin deposits are emplaced within the Rooiberg fragment, a remnant of Transvaal Supergroup sediments and Rooiberg Group rhyolites that was floated up by the emplacement of the magmas of the Bushveld Magmatic Province (BMP) between 2060 and 2050 million years ago (Ma). The source of the fluids that formed the Rooiberg tin deposits were the granites of the Lebowa Granite Suite (LGS) of the BMP, which surround, and are presumed to underlie, the Rooiberg Fragment. LGS granites are dated to 2057 ± 3 Ma by multiple SHRIMP (Selective High Resolution Ion MicroProbe) analyses of single zircons (Kinnaird et al., 2004). Other tin deposits in
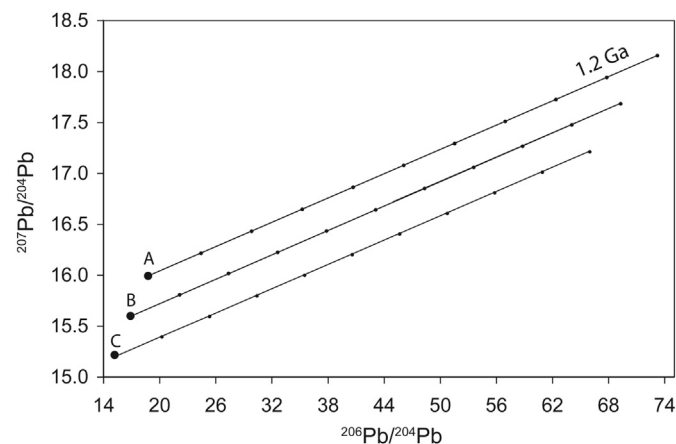

Fig. 2. Three calculated reference isochrons for tin deposits which are all 1.2 billion years old, but formed in isotopically distinct geologic environments. Consequently, each deposit starts with a different "common lead" isotopic signature, indicated by points A, B, and C.

Fig. 3. Map of southeast Africa displaying the location of modern towns (■) and archaeological sites where tin, lead–tin, and bronze artifacts were excavated (∗). Figure provided by Simon Hall.

Southern Africa are hosted in pegmatites, and none date within 300 Myr of the LGS (von Knorring and Condliffe, 1987).

Cassiterite ores were concentrated to very high grade before smelting, so that only a minor amount of slag was produced relative to the amount of tin. The slags were formed by reaction between cassiterite, the residual gangue minerals intergrown with the cassiterite (tourmaline, Fe–Ca–Mg carbonates), and the ends of the tuyeres (ceramic pipes), which protruded into the furnaces and appear to have supplied most of the silica and alumina. The tuyeres are composed of clays naturally tempered with arkose rock fragments (Chirikure et al., 2010). Arkose and shales of the Transvaal form the floor of the Rooiberg valley and are older than the tin ore deposits within them (Rozendaal et al., 1995). Since these sedimentary rocks formed through deposition of materials eroded from still older rocks, the clays derived from arkose and shales in the furnace lining and tuyeres are expected to have different Pb isotopic ratios than the tin ore.

In addition to the tin artifacts and associated smelting materials, 34 bronzes and one copper object were analyzed for Pb isotopes as part of this study. These objects originated from archaeological sites throughout Southern Africa, including Mapungubwe (13th century), Bosutswe (13th–16th centuries), Great Zimbabwe (a late component, 15th–16th centuries) and Thulamela (16th–17th centuries) (see map on Fig. 3) (For descriptions of the objects, see Miller (2002) and Denbow and Miller (2007)).

2.2. Bronze artifacts and ingots from Romania

Four samples of late bronze jewelry and a bronze ingot from the collection of the Arad County History Museum (Romania) were analyzed for Pb isotopes during this study. The jewelry pieces are from well-studied late bronze sites in central Romania (Telnac and Santana), while the ingot is from Spalnaca (north-central Romania) (Macovei and Popescu, 2011). Polished sections of the bronze jewelry samples typically show dendritic textures with various degrees of secondary alteration (malachite) along fractures. Macovei (2011)

showed that the ingot and majority of bronze artifacts from these two localities are extremely heterogenous in terms of their major element compositions, but have a relatively consistent Cu/Sn ratio of approximately 20. The ingot exhibits copper sulfide–magnetite exsolutions under reflected light microscopy. The pieces selected for Pb isotopic measurements did not have measurable Pb using qualitative tools such as a hand-held XRF instrument and micro-PIXE previously applied on these samples (i.e., Pb concentrations <50 mg/kg) (Macovei, 2011). The samples from Romania are of archaeometallurgical interest because no tin ores are known to be present within the nearby Carpathian Mountains. While local copper ore deposits are well documented, including some that were mined back in the Bronze Age (Boroffka, 2006), the origin of tin in these Romanian bronzes remains unresolved.

3. Methods

Material was extracted from all samples using a hand-held electric drill and lead-free tungsten-carbide dental drill bits; a fresh bit was used for each sample. In order to avoid possible surface contamination, samples were immersed in a 1% HNO_3 solution for five to 20 min. Samples were dissolved in 8 M HNO_3 or aqua regia in clean Teflon containers at 125 °C. Subsequently, all aqua regia solutions were dried down in a HEPA filtered environment, and each sample was re-dissolved in 8 M HNO_3. Lead was then separated using Sr-Spec™ resin in Teflon columns (as discussed in Chesley et al., 2002). Total process Pb blanks were run along with samples and were less than 100 pg. Lead isotopic analysis was conducted on a GV Instruments multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the University of Arizona, according to the methods discussed in Thibodeau et al. (2007) and Drew et al. (2009). Data and errors were also calculated according to the methods in Thibodeau et al. (2007) and Drew et al. (2009). External 2-sigma errors associated with each Pb isotopic ratio are reported in Tables 1 and 2. The ^{207}Pb–^{206}Pb regression ages and MSWD (Mean Square of Weighted Deviates) were calculated (using the $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ values and the 2-sigma absolute errors) with Isoplot/Ex3 (Ludwig, 2003). MSWD values qualitatively reflect how well an isochron fits the line. An ideal isochron would give a MSWD value of 1 where regression scatter on the isochron can be explained by analytical uncertainties. A large scatter in the regression not explained by analytical errors yield larger than 1 MSWD values, whereas MSWD values significantly less than 1 indicate that the analytical uncertainties have been overestimated.

Lead concentrations from the initial solutions were measured on an Elan DRC-II ICP-MS instrument at the University of Arizona for all but the Romanian bronzes. These last samples were measured on a Thermo XSeries 2 quadrupole ICP-MS following the procedures reported in Rossel et al. (2013). A subset of un-corroded tin and bronze objects were sampled and dissolved in 8 M HCl, and subsequently diluted for analysis of lead and tin concentrations on the same Elan DRC-II ICP-MS instrument at the University of Arizona (Tables 1 and 2). External errors are reported as the 2-sigma absolute errors in Tables 1 and 2.

4. Results

4.1. Smelted tin

High-precision Pb isotopic measurements were made on seven prehistoric tin ingots, two prehistoric lead–tin ingots, one sample of tin from the last run (1992) of the modern tin smelter at Rooiberg, five tin prills extracted from slags on prehistoric smelting sites in the Rooiberg valley, four of the glassy slags from which prills

Table 1

The measured $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ values for southern African tin, slag, and tuyere samples. Samples run at the same time are grouped together. The lead concentrations (ppm) measured by ICP-MS are also shown (N/A − not analyzed). The two lead−tin ingots are both roughly 80% Pb, 20% Sn, as determined with SEM-EDS by Miller (Miller, 2002; Denbow and Miller, 2007).

Group	Sample name	Sample type	Site where recovered	$^{206}Pb/^{204}Pb$	2σ abs. error	$^{207}Pb/^{204}Pb$	2σ abs. error	$^{208}Pb/^{204}Pb$	2σ abs. error	Pb (mg/kg)
1	14/47/3	Sn ingot	Polokwane area (surface)	24.518	0.011	16.523	0.008	40.439	0.025	86.72
	21/39/1	Sn ingot	Rooiberg valley (surface)	21.787	0.010	16.213	0.008	40.237	0.025	123.06
	14/47/2	Sn ingot	Polokwane area (surface)	18.682	0.008	15.656	0.008	38.429	0.024	211.10
	14/47/1	Sn ingot	Polokwane area (surface)	18.707	0.008	15.654	0.008	38.448	0.024	138.51
	21/39/3	Sn ingot	Rooiberg valley (surface)	91.130	0.041	24.945	0.013	42.002	0.026	9.77
	Lerale	Sn ingot	Soutpansberg mountains (surface)	17.306	0.008	15.643	0.008	37.640	0.023	16.01
	Z581	Sn ingot	Great Zimbabwe	19.577	0.009	15.995	0.008	40.047	0.025	1199.58
	Z334	Sn−Pb lump	Great Zimbabwe	15.111	0.007	15.239	0.008	34.760	0.022	N/A
	SKRT1	Sn prill	Smelterskop (Rooiberg Valley)	19.197	0.009	15.887	0.008	38.002	0.024	54.73
	Sea 5K	Sn prill	Smelterskop (Rooiberg Valley)	18.021	0.008	15.737	0.008	37.745	0.024	297.03
2	Sa-13A	Sn prill	Smelterskop (Rooiberg Valley)	18.371	0.005	15.805	0.005	38.774	0.015	N/A
	Sa-14A	Sn prill	Elandsberg Ledge (Rooiberg Valley)	22.404	0.007	16.199	0.005	42.049	0.016	5.37
	Sa-11A	Sn prill	Elandsberg Ledge (Rooiberg Valley)	49.015	0.014	19.777	0.006	49.581	0.019	6.23
	Sa-1	Sn ingot	Rooiberg − modern smelter	24.551	0.007	16.510	0.005	40.661	0.015	143.36
	Sa-2	Sn ingot	Kamativi − modern smelter	33.422	0.010	16.819	0.005	38.384	0.014	50.85
	Sa-3	Tuyere	Smelterskop (Rooiberg Valley)	22.890	0.007	17.583	0.005	45.380	0.017	N/A
	Sa-4	Tuyere	Smelterskop (Rooiberg Valley)	22.596	0.007	17.033	0.005	45.883	0.017	N/A
	Sa-5R	Tuyere	Smelterskop (Rooiberg Valley)	20.862	0.006	16.007	0.005	41.601	0.016	N/A
	Sa-10	Vitrified Tuyere	Smelterskop (Rooiberg Valley)	33.141	0.010	25.026	0.008	63.320	0.024	N/A
	Sa-6	Slag	Smelterskop (Rooiberg Valley)	19.851	0.006	17.556	0.005	42.375	0.016	N/A
	Sa-11B	Slag paired with Sa-11A	Elandsberg Ledge (Rooiberg Valley)	21.575	0.006	16.253	0.005	42.849	0.016	N/A
	Sa-13B	Slag paired with Sa-13A	Smelterskop (Rooiberg Valley)	21.541	0.006	17.620	0.005	44.273	0.017	N/A
	Sa-14B	Slag paired with Sa-14A	Elandsberg Ledge (Rooiberg Valley)	30.770	0.009	21.619	0.007	58.570	0.022	N/A
	L11	Slag paired with Sea 5K	Smelterskop (Rooiberg Valley)	18.014	0.005	15.729	0.005	37.723	0.014	N/A
	L15	Slag paired with SKRT1	Smelterskop (Rooiberg Valley)	20.191	0.006	16.614	0.005	39.862	0.015	N/A
3	BO1	Sn−Pb lump	Bosutswe	15.114	0.005	15.244	0.004	34.779	0.011	N/A

were extracted, and five samples of tuyeres. All results are reported in Table 1.

The Pb isotopic ratios for tin prills, slags, and tuyeres from two smelting sites at the northern end of the Rooiberg valley are shown in Fig. 4. The four slags are part of matched pairs with four prills (i.e., the prills were drilled out of the slags). Note that: (1) the Pb isotopic ratios of most of the tuyere and slag pieces are very variable but distinctly different from those of the tin prills; and (2) the isotopic ratios of the tin prills are highly variable but fall on a straight line (i.e., an isochron). The calculated $^{207}Pb/^{206}Pb$ age of the tin prill isochron is 2052 ± 34 Ma − a good match to the currently accepted radiometric age (2057 ± 3 Ma; Kinnaird et al., 2004) of the Lebowa Granite Suite, the source of the ore-forming fluids for the Rooiberg tin deposits. We therefore conclude that the tin prills did not pick up significant amounts of lead from either tuyeres or slags during smelting and that the line is a valid "fingerprint" for the Rooiberg tin deposits, to which tin samples of unknown provenance may be compared.

The $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios for all tin objects analyzed are shown on Fig. 5. This includes the tin prills and ingots from Rooiberg smelting sites (Fig. 4), tin from the modern Rooiberg smelter, tin and lead−tin ingots from the archaeological sites various distances from Rooiberg (shown on Fig. 3), and several undated surface finds of tin ingots. For contrast, we also analyzed a sample of tin from the modern smelter at Kamativi, Zimbabwe, which is a pegmatite tin deposit formed during the Kibaran orogeny (900−1100 Ma), and thus about 1000 Myr younger than the Rooiberg deposits (von Knorring and Condliffe, 1987).

The open square symbol at the bottom left of Fig. 5 represents two objects with essentially identical Pb isotopic ratios and very similar chemical compositions (approximately 80% Pb, 20% Sn) (Miller, 2002; Denbow and Miller, 2007). These are the only two lead−tin alloys known from southern Africa prior to European colonization. Both were found in contexts dated by radiocarbon techniques

between 1450 and 1550 cal AD, but at sites (Great Zimbabwe and Bosutswe) that are 500 km apart (Fig. 3) (Miller, 2002). The Pb isotopic ratios of these two objects are obviously those of the lead in the alloy, not the tin, and are much lower than any Pb isotope data yet published from the Bushveld Magmatic Province. It seems probably, therefore, that the lead in these objects came from some other source, so these objects were not included in calculation of any isochrons. The modern tin ingot from Kamativi, Zimbabwe was also excluded from the calculation since it was analyzed as an example of tin that does not originate from the Rooiberg tin deposits.

The Pb isotopic ratios of tin objects not recovered at Rooiberg (shown as circles on Fig 5) define a scattered isochron, with an age of 2196 ± 36 Ma. Although this isochron is only based on 5 data points, it has an age within range of that defined in Fig. 4 for the tin prills and ingots recovered at Rooiberg (Age = 2052 ± 34 Ma). Thus we conclude that all the prehistoric tin objects that we have analyzed with the exception of the two lead−tin alloys derived from the Rooiberg deposits, or from another tin deposit associated with the Lebowa Granite Suite. If we determine an isochron from the Pb isotopic ratios of all of these tin objects (including the tin ingot from the modern Rooiberg smelter, tin prills and ingots recovered at Rooiberg, and tin objects recovered in various archaeological sites and surface locations in Southern Africa), we obtain an isochron age of 2059 ± 36 Ma. Since no evidence of prehistoric mining or smelting has been reported at other LGS tin deposits, the Rooiberg mines are the probable source of all these objects. It is also clear from Fig. 5 that the modern tin sample from Kamativi falls significantly off the isochron, as would be expected of tin originating from a genetically unrelated and younger deposit.

4.2. African bronzes

The Pb isotopic ratios of 34 bronzes from the archaeological sites of Mapungubwe (13th century), Bosutswe (13th−16th centuries),

Table 2
Measured $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ values for southern African bronze and copper samples. Samples run at the same time are grouped together. The lead concentrations (ppm) measured by ICP-MS are also shown (N/A − not analyzed).

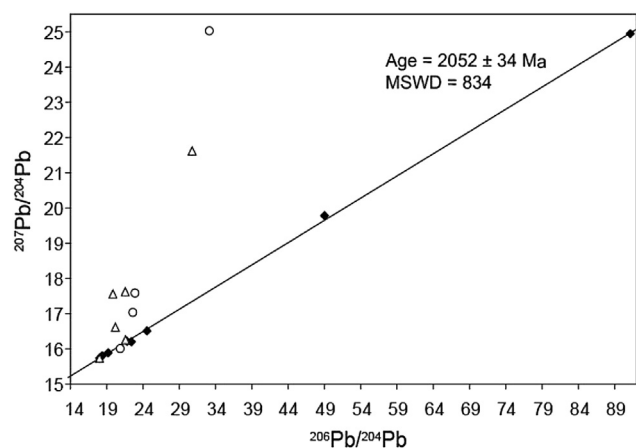| Group	Sample name	Sample type	Site where recovered	$^{206}Pb/^{204}Pb$	2σ abs. error	$^{207}Pb/^{204}Pb$	2σ abs. error	$^{208}Pb/^{204}Pb$	2σ abs. error	Pb (mg/kg)
4	TM 101B	Sn−Cu Bronze	Thulamela	12.951	0.004	14.167	0.004	32.823	0.013	357.00
	TM107	Sn−Cu Bronze	Thulamela	20.452	0.006	16.512	0.005	44.006	0.018	5.32
	TM 101A	Sn−Cu Bronze	Thulamela	47.185	0.014	19.494	0.006	61.245	0.025	49.33
	M336	Sn−Cu Bronze	Mapungubwe	39.243	0.012	18.343	0.006	52.588	0.021	93.27
	M1101	Sn−Cu Bronze	Mapungubwe	18.448	0.006	15.631	0.005	38.453	0.016	N/A
	B136	Sn−Cu Bronze	Bosutswe	66.105	0.020	21.866	0.007	82.214	0.033	44.81
	B86	Sn−Cu Bronze	Bosutswe	20.259	0.006	15.816	0.005	39.131	0.016	N/A
	B96	Sn−Cu Bronze	Bosutswe	18.623	0.006	15.662	0.005	38.605	0.016	14.61
	B316	Sn−Cu Bronze	Bosutswe	19.976	0.006	15.956	0.005	39.348	0.016	24.62
	B3	Sn−Cu Bronze	Bosutswe	19.707	0.006	15.968	0.005	40.027	0.016	N/A
	B61	Sn−Cu Bronze	Bosutswe	17.043	0.005	15.540	0.005	36.326	0.015	N/A
	B26	Sn−Cu Bronze	Bosutswe	18.615	0.006	15.663	0.005	38.603	0.016	N/A
	B85	Sn−Cu Bronze	Bosutswe	18.359	0.006	15.681	0.005	38.353	0.016	N/A
	B393	Sn−Cu Bronze	Bosutswe	19.013	0.006	15.883	0.005	39.278	0.016	N/A
	B394	Sn−Cu Bronze	Bosutswe	19.010	0.006	15.881	0.005	39.272	0.016	N/A
	B451	Sn−Cu Bronze	Bosutswe	18.514	0.006	15.696	0.005	38.804	0.016	N/A
	B471	Sn−Cu Bronze	Bosutswe	18.158	0.006	15.647	0.005	37.783	0.015	N/A
	B486	Sn−Cu Bronze	Bosutswe	36.089	0.011	17.920	0.006	49.225	0.020	N/A
	B470	Sn−Cu Bronze	Bosutswe	18.401	0.006	15.684	0.005	38.627	0.016	N/A
	B466	Sn−Cu Bronze	Bosutswe	23.348	0.007	16.381	0.005	39.888	0.016	N/A
	B461	Sn−Cu Bronze	Bosutswe	18.361	0.006	15.682	0.005	38.358	0.016	N/A
	BST4	Sn−Cu Bronze	Bosutswe	16.572	0.005	15.533	0.005	37.114	0.015	N/A
	BST9	Sn−Cu Bronze	Bosutswe	17.375	0.005	15.628	0.005	36.803	0.015	N/A
	BST6	Sn−Cu Bronze	Bosutswe	19.021	0.006	15.855	0.005	38.620	0.016	N/A
	BST3	Sn−Cu Bronze	Bosutswe	25.415	0.008	16.707	0.005	45.872	0.019	N/A
	B406	Sn−Cu Bronze	Bosutswe	22.349	0.007	16.283	0.005	40.150	0.016	N/A
	B139	Sn−Cu Bronze	Bosutswe	18.461	0.006	15.654	0.005	38.618	0.016	N/A
	B481	Sn−Cu Bronze	Bosutswe	18.910	0.006	15.866	0.005	39.916	0.016	N/A
	BST1	Sn−Cu Bronze	Bosutswe	20.265	0.006	15.983	0.005	38.464	0.016	N/A
	BST2	Sn−Cu Bronze	Bosutswe	17.487	0.005	15.627	0.005	36.837	0.015	N/A
	BST8	Sn−Cu Bronze	Bosutswe	17.503	0.005	15.619	0.005	37.028	0.015	N/A
5	Z428	Sn−Cu Bronze	Great Zimbabwe	26.889	0.007	16.853	0.004	40.267	0.010	N/A
	Z158	Sn−Cu Bronze	Great Zimbabwe	20.401	0.005	16.187	0.004	39.929	0.010	N/A
	Z144	Sn−Cu Bronze	Great Zimbabwe	20.405	0.005	16.189	0.004	39.931	0.010	85.76
	Z10	Cu Artifact	Great Zimbabwe	20.909	0.005	16.434	0.004	41.729	0.010	N/A
6	BBD 10	Cu Prill	Rooiberg Blaauwbank	16.459	0.004	15.487	0.003	36.490	0.011	N/A
	BBD 3	Cu Rod	Rooiberg Blaauwbank	16.935	0.004	15.507	0.003	37.716	0.011	N/A
	BBD 11	Cu Prill	Rooiberg Blaauwbank	18.262	0.004	15.790	0.003	38.324	0.011	N/A
	BBD 12	Cu Prill	Rooiberg Blaauwbank	16.050	0.004	15.438	0.003	35.983	0.011	N/A
	BBD M1	Cu Ore	Rooiberg Blaauwbank	17.386	0.004	15.571	0.003	38.677	0.012	N/A
	VEL M1	Cu Ore	Rooiberg Vellefontein	15.465	0.003	15.310	0.003	35.485	0.011	N/A
	BBD M3	Cu Ore	Rooiberg Blaauwbank	17.758	0.004	15.618	0.003	39.295	0.012	N/A

Fig. 4. Lead isotopic ratios of tuyeres (○), slags (△), and tin prills and ingots (◆) from two prehistoric smelting sites adjacent to the Rooiberg tin deposits. The fitted isochron was calculated using only the isotopic values for the tin prills and ingots. Two-sigma analytical errors are in all cases smaller than the symbols used.
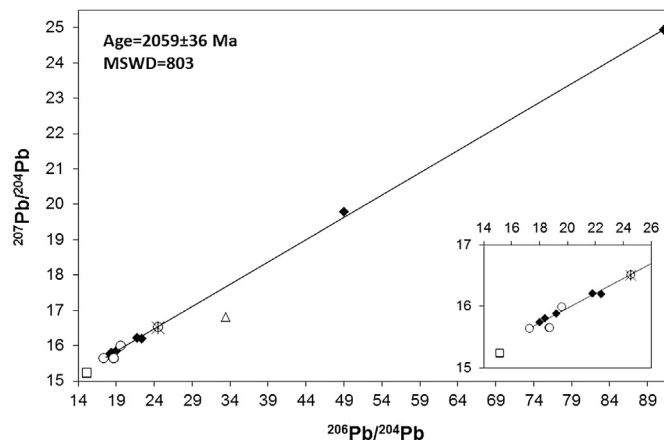

Fig. 5. Lead isotopic ratios of prehistoric tin ingots & prills from southern Africa (◆), modern Rooiberg tin (*), and Bosutswe and Great Zimbabwe lead−tin ingots (□). The modern tin ingot from Kamativi, Zimbabwe (△) and the lead−tin ingots were not included in the calculation of the fitted isochron. Two-sigma analytical errors are in all cases smaller than the symbols used.
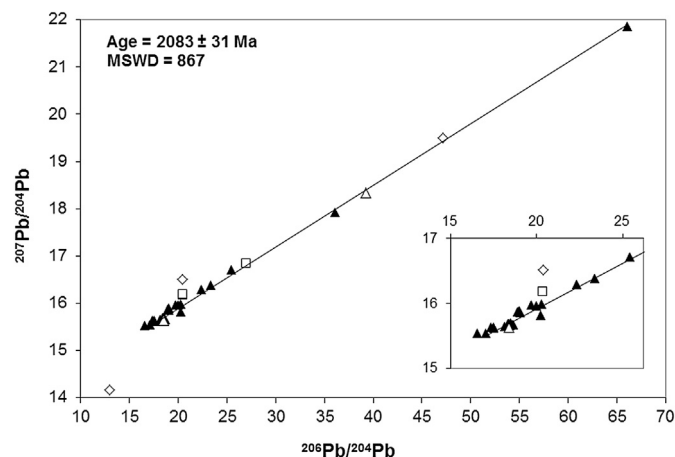
Fig. 6. Lead isotopic ratios for Bosutswe bronze objects (▲), Thulamela bronze objects (◇), the Mapungubwe bronze objects (△), and the Great Zimbabwe bronze objects (□). Two of the Thulamela bronzes diverge from the fitted isochron, as do two of the Great Zimbabwe bronzes (which plot directly on top of one another). These were not included in the age calculation. Two-sigma analytical errors are in all cases smaller than the symbols used.
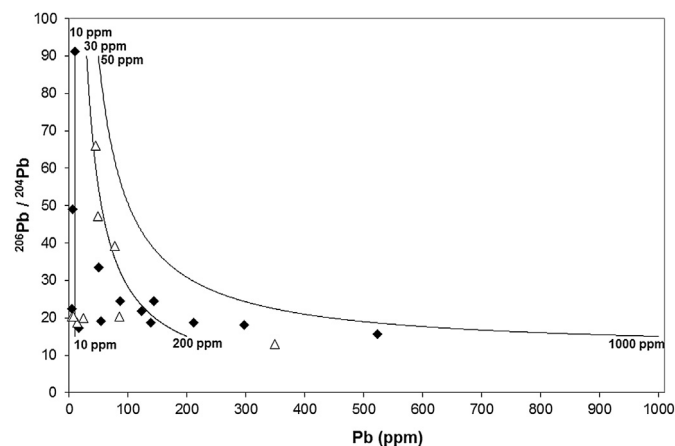

Fig. 7. The $^{206}Pb/^{204}Pb$ ratios and lead concentrations for southern African tin samples (◆) and bronzes (△). The lines represent hypothetical mixtures of cassiterite containing 10, 30 and 50 ppm Pb with sulfide minerals containing 10, 200, and 1000 ppm Pb.

Thulamela (16th–17th centuries), and Great Zimbabwe (15th–16th centuries) are listed in Table 2 (For descriptions of the objects, see Miller (2002) and Denbow and Miller (2007)). The locations of these sites are shown in Fig. 3. A plot of $^{207}Pb/^{204}Pb$ against $^{206}Pb/^{204}Pb$ for the 34 bronze artifacts (Fig. 6) shows that about four-fifths of the samples display a strong linear trend, and that about one-fourth of the samples analyzed have radiogenic isotopic ratios ($^{206}Pb/^{204}Pb > 22$). As copper ores generally possess "common lead" isotopic ratios, we suggest that these radiogenic signatures are contributed by the tin in the alloy (Lambert and Ruiz, 1999).

Four bronzes (two from Thulamela and two from Great Zimbabwe) do not lie on the linear trend. We excluded these four samples in the calculation of an isochron, which gave an age of 2083 ± 31 Ma and a MSWD of 867. This isochron is identical within error to the isochron calculated for the tin artifacts (Fig. 4).

Lead and tin concentrations were determined for several non-corroded bronzes with radiogenic ($^{206}Pb/^{204}Pb > 22$) and common lead ($^{206}Pb/^{204}Pb < 22$) isotopic signatures, including the two Thulamela bronzes that did not lie on the model isochron in Fig. 6. The tin contents of the analyzed bronzes ranged from <1% to ~7%, and as shown on Fig. 7, all analyzed bronzes but one from Thulamela (TM101B) have lead concentrations less than 100 ppm. The significantly higher lead concentration (>300 ppm Pb) of the Thulamela bronze and its notably low $^{206}Pb/^{204}Pb$ isotopic ratio ($^{206}Pb/^{204}Pb < 15$) suggests that the copper and/or tin ore used in its fabrication originated from a different source than the Lebowa Granite Suite, and that its Pb isotopic signature is dominated by "common lead".

4.3. Romanian bronzes

Lead isotopic ratios and analytical errors for the five Romanian bronze samples are given in Table 3, together with Pb concentrations. Compared to analyzed regional ore deposits from the nearby South Carpathians and the Apuseni Mountains (Macovei, 2011), the five analyzed bronzes have slightly higher (i.e., more radiogenic) Pb isotopic ratios and define a 305 ± 102 Ma $^{207}Pb-^{206}Pb$ isochron (Fig. 9). Of the five bronzes, the more radiogenic Pb isotopic ratios are correlated with lower concentrations of Pb. The apparent ~300 Ma age defined in the isochron is Variscan − a late Paleozoic orogenic event that affected most of the metamorphic basement rocks in continental Europe. With the exception of tin sources from Scandinavia, Variscan basement rocks are the primary source of tin ore in antiquity in central Europe. Particularly important Variscan tin deposits are located in Cornwall, England and Erzgebirge (Bohemian Massif) in the Czech Republic. The Romania data presented here cannot be used to fingerprint the source of tin in detail. However, this data is significant in that the apparent ~300 Ma age defined in the isochron rules out a nearby origin for the tin in the Carpathians Mountains, which contain much younger ore deposits (late Cretaceous to Miocene, Borcoş et al., 1998).

5. Interpretations

5.1. Isochrons and mixing lines

Here we address the possibility that the isochrons calculated from the tin objects may, in fact, represent mixing lines between the Pb isotopic signatures of common lead minerals and the radiogenic Pb isotopic signatures of cassiterite. Low-temperature tin deposits like Rooiberg usually contain sulfides as well as cassiterite (Taylor, 1979). In the Rooiberg tin deposits, pyrite is the most common sulfide mineral, with very minor amounts of chalcopyrite and galena (Leube and Stumpfl, 1963; Crocker et al., 2001; Labuschagne, 2004). Because the sulfides and cassiterite in the Rooiberg deposit crystallized from the same hydrothermal fluids, it

Table 3
Measured $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ and Pb concentration values for Romanian bronze samples, with percentage 2-sigma errors (analytical description in text).

Sample name	Sample type	Site where recovered	$^{206}Pb/^{204}Pb$	2σ abs. error	$^{207}Pb/^{204}Pb$	2σ abs. error	$^{208}Pb/^{204}Pb$	2σ abs. error	Pb (mg/kg)
P35	Nail	Felnac	18.442	0.004	15.735	0.004	38.606	0.012	19.00
P4	Reap	Santana	18.254	0.006	15.727	0.004	38.491	0.018	18.44
P8	Bracelet	Santana	18.320	0.004	15.732	0.006	38.524	0.012	14.53
P20	Disk	Cicir	18.881	0.004	15.762	0.006	39.226	0.022	9.07
P36	Ingot	Spalnaca	19.557	0.006	15.795	0.005	39.654	0.016	4.12
P9	Ingot	Santana	19.234	0.040	15.778	0.005	39.443	0.014	6.33

Table 4
The $^{206}Pb/^{204}Pb$, and $^{207}Pb/^{206}Pb$ values along with their corresponding absolute 2-sigma errors for pure copper and all Sn-bronze objects from Al Soufouh, Unar1, Unar2, and Tell Abraq in Oman, from Table 7.1 in Weeks (2003). The $^{207}Pb/^{204}Pb$ values are calculated by us from these data, and the corresponding absolute 2-sigma errors are assumed to be the same as those for$^{206}Pb/^{204}Pb$ values.

Sample	Site	Major elements	$^{207}Pb/^{206}Pb$	2σ abs. error	$^{206}Pb/^{204}Pb$	2σ abs. error	$^{207}Pb/^{204}Pb$
M10-41	Al Sufouh	Cu	0.847	0.000	18.525	0.005	15.683
M10-38	Unar1	Cu	0.850	0.000	18.378	0.002	15.614
1019-3.59	Unar2	Cu	0.873	0.000	17.997	0.004	15.709
TA1227	Tell Abraq	Cu	0.841	0.000	18.671	0.001	15.695
TA1310	Tell Abraq	Cu	0.837	0.000	18.804	0.002	15.730
TA1461	Tell Abraq	Cu	0.841	0.000	18.699	0.001	15.724
AS1-2	Al Sufouh	Cu−As−Sn (low)	0.885	0.000	17.747	0.003	15.701
ASTombid	Al Sufouh	Cu−Sn(low)−As−Ni	0.851	0.000	18.485	0.003	15.727
M10-7	Unar1	Cu−Sn(low)	0.850	0.000	18.451	0.001	15.686
M10-13v	Unar1	Cu−Sn	0.849	0.000	18.461	0.004	15.668
M10-17 Avg.	Unar1	Cu−Sn(low)	0.813	0.000	19.392	0.005	15.772
M10-19	Unar1	Cu−Sn(low)	0.855	0.000	18.299	0.002	15.653
M10-22r	Unar1	Cu−Sn−Fe	0.852	0.000	18.330	0.003	15.626
M10-39	Unar1	Cu−Sn−Fe	0.849	0.000	18.372	0.002	15.601
1014.76	Unar2	Cu−Sn−As	0.863	0.000	18.167	0.004	15.678
1014.158	Unar2	Cu−Sn−As	0.868	0.000	18.055	0.002	15.678
1018-3.99	Unar2	Cu−Sn−As−(Ni)	0.844	0.000	18.615	0.002	15.711
1019-5.71	Unar2	Cu−Sn−As	0.843	0.000	18.655	0.003	15.723
1023-4.10	Unar2	Cu−Sn−(Fe)	0.854	0.000	18.404	0.004	15.723
1019-3.105	Unar2	Cu−Sn−As−Fe	0.873	0.000	18.028	0.004	15.740
1023-2.110	Unar2	Cu−Sn(low)−Fe	0.893	0.000	17.507	0.003	15.637
TA107 Avg.	Tell Abraq	Cu−Sn−As−Ni	0.818	0.000	19.244	0.001	15.742
TA699 Avg/	Tell Abraq	Cu−Sn	0.660	0.000	24.401	0.003	16.102
TA1217	Tell Abraq	Cu−Sn	0.834	0.000	18.831	0.003	15.709
TA1231	Tell Abraq	Cu−Sn(low)	0.871	0.000	18.061	0.001	15.726
TA1286	Tell Abraq	Cu−Sn	0.835	0.000	18.792	0.002	15.691
TA1306	Tell Abraq	Cu−Sn	0.835	0.000	18.807	0.001	15.711
TA1428	Tell Abraq	Cu−Sn(low)−Fe	0.847	0.000	18.515	0.001	15.684
TA1459	Tell Abraq	Cu−Sn	0.846	0.000	18.531	0.001	15.681
TA1614 Avg.	Tell Abraq	Cu−Sn−Fe	0.634	0.000	25.518	0.010	16.176
TA1648	Tell Abraq	Cu−Sn	0.874	0.000	17.919	0.001	15.667

is expected that they would possess the same initial "common lead" isotopic signature. However, as stated previously, while the sulfide minerals will retain that common lead signature, the Pb isotopic signatures of the cassiterite crystals will evolve over time due to the radioactive decay of U or Th.

As noted in Chirikure et al.'s (2010) paper on the technology of prehistoric tin smelting at Rooiberg, cassiterite was concentrated before smelting, almost certainly by panning in water. Any galena present would be retained with cassiterite. Some fraction of the pyrite and other sulfide minerals might also be retained in the panned concentrate. Depending on the percentage of sulfide minerals incorporated into the tin smelt, and the Pb content of the minerals (e.g., galena, which typically contains ~800,000 ppm vs.

pyrite which can contain Pb concentrations ranging several orders of magnitude), the smelted tin object will possess a Pb isotopic signature somewhere along a mixing line between the cassiterite and the sulfide mineral.

To show this graphically, the $^{206}Pb/^{204}Pb$ values of several of the tin samples have been plotted against their measured Pb concentrations in Fig. 7 (tin objects are shown as black diamonds). Superimposed on this plot are three calculated mixing lines between cassiterite (for which a radiogenic $^{206}Pb/^{204}Pb$ ratio of 90 is assumed) and a hypothetical assortment of sulfide minerals that may have been inadvertently added to the tin smelt (for which a common lead $^{206}Pb/^{204}Pb$ ratio of 15 is assumed). The lines represent hypothetical mixtures of cassiterite containing 10, 30 and 50 ppm Pb with sulfide minerals containing 10, 200, and
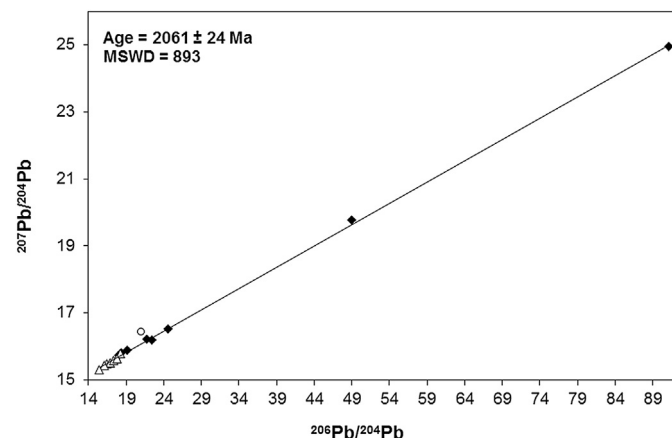

Fig. 8. Lead isotopic ratios for prehistoric tin ingots & prills from southern Africa (◆), copper objects and copper ore from Rooiberg (△), and the Great Zimbabwe copper object (○).
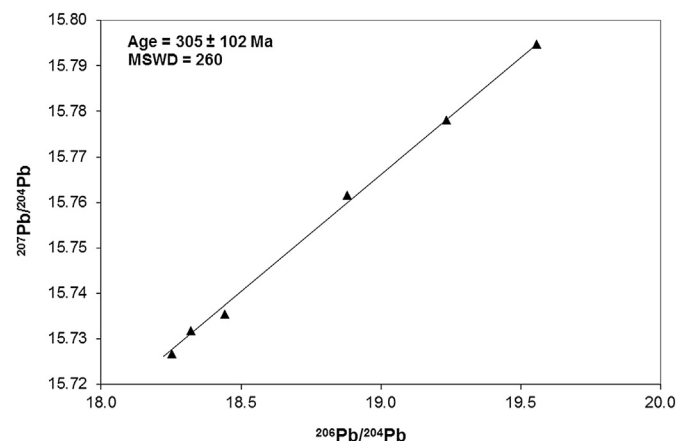

Fig. 9. Lead isotopic ratios and the Pb–Pb isochron of the five Romanian low Pb bronze samples (see description in text).

1000 ppm Pb. Almost all of the tin objects fall between the mixing lines which contain 10 and 50 ppm concentrations of Pb in the cassiterite, indicating that these are the most likely range of Pb concentrations in Rooiberg cassiterite.

While Fig. 7 illustrates that the Pb isotopic signatures of the tin objects likely represent a mixture of the Pb isotopic ratios of both the cassiterite and sulfide minerals entrained in the tin smelt, they still fall on a single line that reflects the known geological age of the Rooiberg deposits. This is true because both the sulfide and cassiterites formed from the same hydrothermal fluids with the same initial "common lead" isotopic ratios. We therefore acknowledge that in this instance, the observed Pb isotopic ratios of the tin objects represent both a mixing line and an isochron. This phenomenon may be observed in the Pb isotopic ratios of tin objects from a variety of archaeological contexts, as the gangue sulfide ore minerals unintentionally incorporated in tin smelts most likely originate from the same deposit as the cassiterite ore.

5.2. Identifying tin sources in bronzes

In light of the discussion of mixing lines it is quite surprising that the isotopic contribution of Rooiberg tin is so evident in the African bronzes. We would expect the Pb isotopic ratios of any unleaded bronze (i.e. a bronze whose lead derives only from lead originally present in the copper and the tin) to lie on a mixing line between the common Pb isotopic signature of the copper component, and the radiogenic Pb isotopic signature of the tin component. The fact that this set of bronzes produces a model geological age that matches that of the Rooiberg tin deposits strongly suggests that (1) both the copper and tin components derived from deposits related to emplacement of the Lebowa Granite Suite (2057 ± 3 Ma) and (2) the copper contained relatively little lead.

There are at least eleven small copper deposits within the Rooiberg Fragment that are genetically related to the LGS (Rozendaal et al., 1995; Henry and Wilson, 2006). We measured Pb isotopic ratios on five pieces of smelted copper from surface scatters in the Rooiberg valley, and on three pieces of arsenical copper ore from one of these copper deposits. For comparison we also analyzed one piece of copper from Great Zimbabwe. The results are given in Table 2, and plotted with the tin prills from Rooiberg smelting sites in Fig. 8. If treated as an isochron, this gives a model age of 2061 ± 24, with MSWD of 893, which is well within error of the geologic age of the Lebowa Granite Suite. Isotopic ratios of the Zimbabwe copper artifact fall notably off this line.

As with the tin, the scatter (MSWD) of the data around the calculated isochron for the bronzes is high, and is indicative of non-analytical scatter in the initial Pb isotopic ratios. In geochronology, isochrons are calculated from isotopic ratios obtained on un-weathered minerals within a single rock or ore, which is assumed to have crystallized at the same time from an isotopically homogenous fluid. The tin artifacts analyzed were likely smelted from cassiterite concentrates that included other minerals, and may have originated from any of the four separate clusters of known prehistoric tin mines in the Rooiberg valley (Baumann, 1919). Because these mines may have contained slightly heterogeneous initial Pb isotopic ratios, resulting from crustal and fluid mixing at a local scale, there might have been slight systematic differences in the initial Pb isotopic ratios between them, as in tin granites from Cornwall (Chesley et al., 1993). The same can be said for the copper deposits.

Consequently, the high MSWDs are probably attributable to: (1) the low number of samples; (2) the high precision of the analyses (ironically, lower analytical error can result in a larger MSWD, since the smaller 2-sigma errors do not in many cases intersect the fitted line); (3) the possibility that the tin may derive from cassiterite

from different deposits within the LGS; and (4) the addition of "common lead" from copper sources and gangue minerals that have slightly different Pb isotopic ratios.

5.3. Tin provenance

The application of isochron methodology is presented as a new geochemical approach to provenance studies of tin and bronze. We have shown that under favorable conditions, isochrons can be effective in determining the source of tin in bronzes. Specifically, the isochron approach may be applied to bronzes that (1) display radiogenic Pb isotopic signatures ($^{206}Pb/^{204}Pb > 22$) and (2) have very low Pb concentrations. In addition to the examples from Southern Africa and Romania discussed above, we have re-plotted data originally published by Weeks (2003) for copper and bronze artifacts from Oman, which are dated between 2400 and 1900 BC (Fig. 10, Table 4). Note that two of these bronzes are radiogenic and have low lead concentrations. An isochron calculated on these two points alone returns a model age of 804 ± 270 Ma. Although this is only a two point isochron and has large errors, Fig. 10 indicates that these bronzes were made with tin from an old ore deposit, which has a neo-Proterozoic age (see Fig. 1). Consequently, these data exclude the possibility that the tin in these two bronzes derived from major Afghan deposits, which were emplaced around 80 Ma (Ludington and Peters, 2007) and thus have not had time to accumulate radiogenic Pb. More likely candidates would be the cassiterite deposits of India, which formed between 700 and 1500 Ma (Babu, 1994).

For the Romanian bronzes, the apparent Variscan age defined by the isochron rules out exotic tin origins (Asia, Middle East, or Africa). In addition, the Variscan age precludes a tin origin in local deposits, as all nearby ores (Cu, Au, Ag, Pb) that could have contained Sn as a secondary mining target (Borcoş et al., 1998) are associated with either Jurassic, Cretaceous or Miocene magmatism (i.e., all part of the "Alpine" orogenesis, younger than the Variscan). While Variscan rocks are common basement units in the Carpathian Mountains (Medaris et al., 2003), no cassiterite ores are know from this area. However, there are well known Variscan tin deposits in central Europe (e.g., the Erzgebirge, also known as the Bohemian Massif), or as far away as the Iberian Peninsula or England. Therefore, by process of elimination, our data most strongly suggest a central/western European origin for the tin in the Romanian bronzes. This preliminary data on Romanian bronzes supports the possibility that tin extracted from cassiterite outside of the early Proterozoic province of
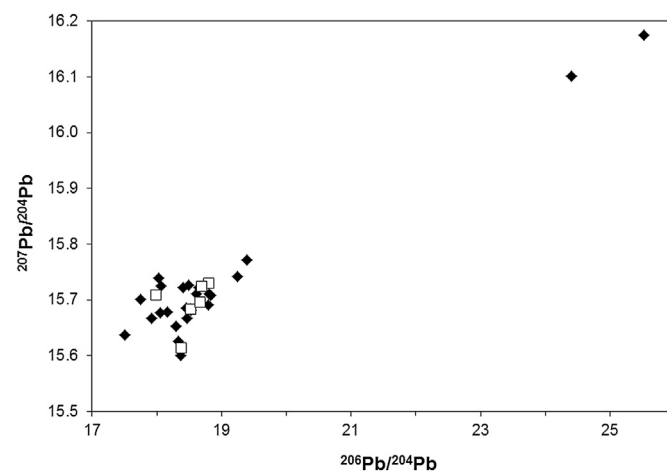

Fig. 10. Lead isotopic ratios of bronzes (◆) and unalloyed copper (□) from Omani Early Bronze sites (from Table 3; Weeks, 2003). Two-sigma analytical errors are in all cases smaller than the symbols used.

South Africa can carry information on the age of the parent ore deposit locked within bronze artifacts.

Globally there are several important cassiterite provinces that could have contributed to the tin budget of ancient bronze artifacts of the Old World: the Afghan, Indian, Malaysian, southern African, and central European tin metallogenetic provinces. The major Afghan tin deposits are too young to be identified by radiogenic Pb isotopic ratios (Ludington and Peters, 2007). Those of India are between 700 and 1500 Ma (Babu, 1994), while those of western peninsular Malaysia are 184–230 Ma (Schwartz et al., 1995). Tin deposits from Europe are mostly Variscan (350–280 Ma) in age and include those of Cornwall (Britain), the Erzgebirge (Germany and Czech Republic), and the Iberian Massif (Portugal and Spain) (Taylor, 1979; Guilbert and Park, 1986). While it may be impossible to distinguish among individual deposits, many of the tin provinces used in bronze artifacts have the potential of being positively identified or ruled out with the method presented here.

6. Conclusions

We present a new approach to determining the provenance of tin, whereby Pb isotopic isochrons obtained from smelted tin may serve as "fingerprints" of cassiterite deposits, and the provenance of tin artifacts can be inferred by matching their isotopic ratios to the isochrons of cassiterite deposits. Lead isotope ratios in bronze can be indicative of the source of tin in the alloy. Any bronze that has both a radiogenic Pb isotope signature and a low Pb content would be worth further investigation by the methods discussed in this article. This approach will be particularly useful in identifying old tin sources (Paleozoic and older), such as those in India, Africa, and much of Europe, and can serve to rule out certain metallogenetic provinces as sources of tin in ancient bronzes.

Acknowledgments

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